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# EVALUATION OF CONTINUOUS COLORIMETRIC METHOD FOR MEASUREMENT OF NITROGEN DIOXIDE IN AMBIENT AIR

John H. Margeson, et al

Environmental Protection Agency
Triangle Park, North Carolina

April 1975

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# EVALUATION OF A CONTINUOUS COLORIMETRIC METHOD FOR MEASUREMENT OF NITROGEN DIOXIDE IN AMBIENT AIR

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16. ABSTRACT

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The results show that static calibration is unreliable; dynamic calibration using a reliable $NO_2$-generation system is required. Ozone was found to be a significant negative interferent.

A detailed method write-up, based on dynamic calibration specifications, was prepared to describe the use of the continuous colorimetric procedure.

The results of a collaborative test ot this method will be the subject of a separate report.

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# EVALUATION OF A CONTINUOUS COLORIMETRIC METHOD FOR MEASUREMENT OF NITROGEN DIOXIDE IN AMBIENT AIR

by

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Program Element No. 1HA327
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Office of Research and Development
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# ABSTRACT

A continuous colorimetric procedure for the measurement of nitrogen dioxide in ambient air was evaluated. The evaluation included laboratory experiments, using two different azo-dye-forming absorbing solutions in a Technicon instrument, to test the reliability of calibration techniques. Other procedures that are important in the use of the method were evaluated, and a literature search was conducted to identify possible interferents.

The results show that static calibration is unreliable; dynamic calibration using a reliable $NO_2$-generation system is required. Ozone was found to be a significant negative interferent.

A detailed method write-up, based on dynamic calibration specifications, was prepared to describe the use of the continuous colorimetric procedure.

The results of a collaborative test of this method will be the subject of a separate report.

# CONCLUSIONS

The information developed as a result of this evaluation was sufficient to allow preparation of the detailed method write-up on the use of a continuous colorimetric method for $NO_2$ measurement that appears in the Appendix. The major conclusions of the evaluation are that dynamic calibration is required and that ozone is a significant negative interferent. The procedures recommended by the Technicon Corporation, manufacturer of the instrument used in this test, do not meet these requirements, in that static calibration is recommended.

# I. INTRODUCTION

On July 14, 1972, the Administrator of the U.S. Environmental Protection Agency withdrew the EPA-promulgated[1] reference method for measuring atmospheric concentrations of nitrogen dioxide ($NO_2$) because of demonstrated inadequacies in the procedure. Research conducted both within[2] and outside[3] EPA revealed that the collection efficiency of the promulgated method varied and that a positive nitric oxide (NO) interference occurred. After the withdrawal, EPA selected three tentative procedures[4] to replace the original method: a continuous colorimetric (Saltzman) procedure, a continuous chemiluminescence procedure, and a manual arsenite procedure.

The report presents the results of an evaluation of the continuous colorimetric procedure by the Methods Standardization and Performance Evaluation Branch (MSPEB) of the Quality Assurance and Environmental Monitoring Laboratory (QAEML). A detailed description of the procedure is given in the Appendix.

Within EPA, MSPEB is responsible for standardizing the measurement methods used in determining compliance with the national ambient air quality standards for various pollutants. This standardization process includes the development of a method description (write-up) that is clearly written and technically accurate based on a combination of literature review, review of existing write-ups, and laboratory evaluation of the procedure.

If a method proves to be reliable after the above evaluation, it can be subjected to a collaborative test designed to determine

its precision (repeatability and reproducibility) and its accuracy (bias). The collaborative test is the final phase of the standardization process and is a measure of the performance of the method in actual use.

# II. EXPERIMENTAL

The specific reagents, the method of preparation of the absorbing solutions, and the dynamic calibration procedures used in the laboratory evaluation were the same as those described in the method write-up (see Appendix). Other pertinent experimental details not contained in the write-up are described in the following paragraphs.

## GENERATION OF DYNAMIC $NO_2$ ATMOSPHERES

Nitrogen dioxide atmospheres were generated using a permeation device and known amounts of clean dilution air. This procedure (Figure A-1) has been described by O'Keeffe and Ortman[5] and Scaringelli et al.[6, 7]

The FEP-Teflon-sleeve, glass-reservoir permeation device (No. 16-3) developed by the National Bureau of Standards (NBS) and EPA was used as the test source of nitrogen dioxide.[8]

This device was calibrated gravimetrically[9] and had a permeation rate of 1.233 ± 0.005 μg $NO_2$/min (95 percent C.I.) at 25.2 ± 0.1 °C. The constancy of the permeation rate for this device was established as shown by the data in Figure 1.

The temperature of the device was controlled by a water-jacketed condenser, which was maintained at 25.2 ± 0.1 °C by a constant-temperature bath (Forma Temperature, Jr.). The $NO_2$ was flushed from the condenser with extra-dry-grade nitrogen at approximately 50 $cm^3$/min after it had passed through a column of molecular sieve (6-16 mesh, type 4-A) and indicating Drierite.

The dilution air used in the test was compressed house air that had been passed through an air filter (Wilkerson Corporation

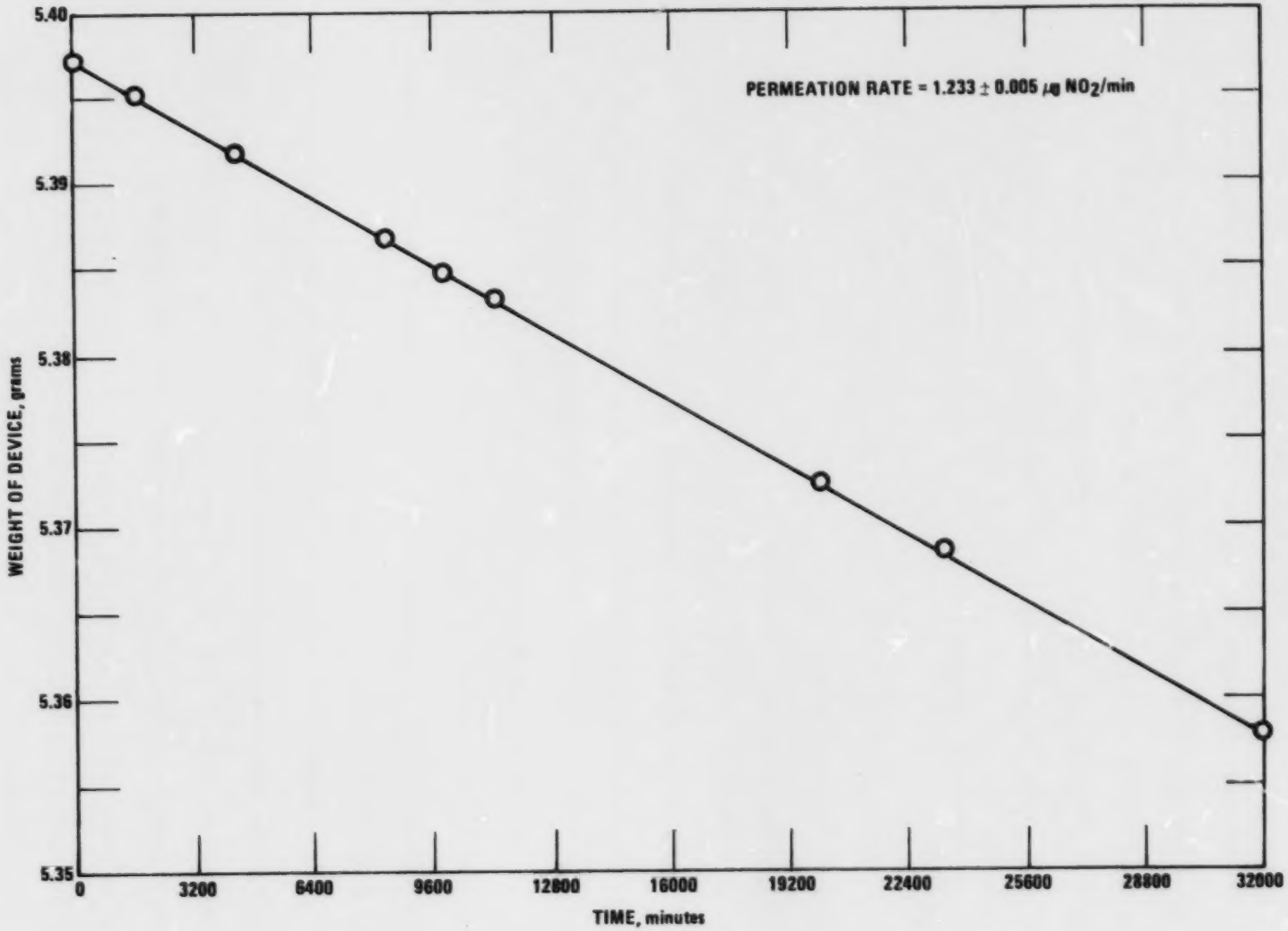


Figure 1. Nitrogen dioxide - permeation rate of NBS-EPA Device No. 16-3.

Model No. 1237-2F) to remove dirt particles and aerosols, though indicating silica gel (6-16 mesh) for drying, through treatment with ozone ($O_3$) to convert NO to $NO_2$, and finally through activated charcoal (6-16 mesh) to remove $NO_2$ and hydrocarbons.

A blank, consisting of a 24-hour sampling of dilution air plus flushing nitrogen with no permeation device in the system, showed a $NO_2$ concentration of less that 2 μg $NO_2/m^3$. Thus, the generation system was free from interferences.

The concentration of $NO_2$ generated was calculated as described in the Appendix.

## STATIC GENERATION OF $NO_2$

The static generation of $NO_2$ was accomplished by adding known concentrations of $NaNO_2$ to the different absorbing reagents. The $NO_2$ concentration was calculated as follows:

1. The $NO_2$ equivalence of the stock $NaNO_2$ solution was:

$$\frac{0.0812 \text{ g } NaNO_2}{1000 \text{ ml}} \times \frac{1 \text{ μl } NO_2}{2.03 \times 10^{-6} \text{ g } NaNO_2} = 40 \text{ μl } NO_2/\text{ml} \qquad (1)$$

2. The $NaNO_2$ to $NO_2$ conversion factor used in equation 1 was derived as follows:

By the ideal gas law, 1 mole of $NO_2$ would occupy a volume of 24.47 ℓ at 25.0 °C and 760 mm Hg. Therefore, $10^{-6}$ moles $NO_2 = 24.47 \times 10^{-6}$ ℓ $NO_2$.

$$\frac{10^{-6} \text{ moles } NO_2}{24.47 \times 10^{-6} \text{ ℓ } NO_2} \times \frac{0.72 \text{ mole } NO_2^- \ ^{12}}{\text{mole } NO_2} \times \frac{69.0 \text{ g } NaNO_2}{\text{mole } NO_2^-} = \frac{2.03 \times 10^{-6} \text{ g } NaNO_2}{\mu\text{l } NO_2} \quad (2)$$

3. This procedure, which is the one recommended by Technicon,[10] assumes 100 percent collection efficiency for $NO_2$ and quantitative conversion of $NO_2^-$ to azo dye. Side reactions resulting in nitric oxide generation have been shown to occur in this reaction.[11]

Calibration standards were prepared by adding different volumes of working $NaNO_2$ solution to 100 ml of absorbing solution to produce the desired levels of $NO_2$. The volume to be added was calculated from the following relationship:

$$\frac{1.6 \text{ } \mu\text{l } NO_2}{\text{ml}} \times \frac{\text{Volume of working solution}}{100 \text{ ml}} \times \frac{\text{Solution flow rate, ml/min}}{\text{Air flow rate, ℓ/min}} = \frac{NO_2 \text{ } \mu\text{l}}{\text{ℓ}} = NO_2 \text{ ppm} \quad (3)$$

REAGENTS

1. $NaNO_2$. ACS reagent grade $NaNO_2$ having an assay of 99.9 percent was dried for 1 hour at 105 °C before use.

2. Stock $NaNO_2$ solution (40 µl $NO_2$/ml). Dry $NaNO_2$ (0.081281 g) was dissolved in distilled water and diluted to 1 ℓ in a volumetric flask. The concentration was adjusted for less than 100 percent assay.

3. Working $NaNO_2$ solution (1.6 µl $NO_2$/ml). Ten ml of stock solution was diluted to 250 ml with distilled water.

## CONTINUOUS COLORIMETRIC INSTRUMENTS

Two Technicon IV Air Monitors were used. The plumbing (air and solution flow rates) of one was modified to allow use of the Saltzman absorbing solution. The other instrument was not modified and was used with the Lyshkow absorbing solution, for which the Technicon IV was designed. The Saltzman absorbing solution contains 0.5 percent sulfanilic acid, 5.0 percent acetic acid, and 0.005 percent N-(1-Naphthyl)-ethylenediamine dihydrochloride (NEDA). The Lyshkow absorbing solution contains 0.15 percent sulfanilamide, 1.5 percent tartaric acid, 0.005 percent NEDA, and 0.005 percent 2-naphthol-3,6-disulfonic acid disodium salt. The procedures used to prepare these aqueous absorbing solutions are given in the Appendix, sections 6.8.1 and 6.8.2.

The operating procedures recommended by the manufacturer were followed in using the instruments. This included maintaining the ratio of the air flow rate to the solution flow rate at 1050. Typical examples of flow rates used with the Lyshkow absorbing solution were 316 $cm^3$/min (air flow rate) and 0.301 $cm^3$/min (solution flow rate); with the modified Saltzman absorbing solution, typical values were 390 $cm^3$/min (air flow rate) and 0.370 $cm^3$/min (solution flow rate).

## TEMPERATURE CYCLING OF ABSORBING SOLUTIONS

Temperature cycling was carried out by immersing the solutions in a constant-temperature bath (Forma Temperature Jr.) and manually adjusting the temperature.

## WAVELENGTH OF MAXIMUM ABSORBANCE

The wavelength of maximum absorbance was determined manually with a spectrophotometer (Beckman Model B).

# III. RESULTS AND DISCUSSION

Continuous colorimetric methods for measuring $NO_2$ are based on absorption of $NO_2$ from the air into an acid solution containing a diazonium salt precursor and a coupling agent. A dye is produced and the color intensity, which is directly proportional to the $NO_2$ concentration, is measured in a colorimeter. The resulting electrical signal is then transmitted to a recorder where the concentration is determined from the recorder chart and the calibration curve.

Absorbed $NO_2$ is first converted to nitrous acid (HONO). The HONO then reacts with e.g., sulfanilic acid to produce a diazonium salt, which then couples with N-(1-Naphthyl)-ethylenediamine dihydrochloride (NEDA) to produce a pink azo dye. Saltzman[12] first recognized that this reaction could be applied to determine $NO_2$ levels in the atmosphere. He developed a manual procedure using an absorbing solution of sulfanilic acid, NEDA, and acetic acid. Thomas[13] developed an apparatus for continuous determination of $NO_2$ using the Saltzman reagent. Saltzman[14] modified the original absorbing solution, mainly by reducing the acetic acid concentration. Lyshkow[15, 16] reduced the instrument response time to less than one minute by adding a disodium sulfonate to a Saltzman-type absorbing solution.

Users of continuous colorimetric methodology for $NO_2$ measurements indicate that both the modified Saltzman and Lyshkow absorbing solutions are being used. Accordingly, both were included in this evaluation.

Because it would be prohibitive from a time-cost standpoint to evaluate all of the available continuous colorimetric instruments with the two absorbing solutions, the MSPEB evaluation used one rather popular instrument, the Technicon IV.

## DYNAMIC VERSUS STATIC CALIBRATION

An accurate calibration of any method is, of course, extremely important. Dynamic procedures are generally preferred over static ones because the former simulates actual use conditions whereas the latter does not. Both procedures are in use, however, with continuous colorimetric methods for $NO_2$. Because Technicon recommends static calibration,[10] it was decided to compare static calibration with an accurate dynamic procedure as a reference.

A reliable $NO_2$ permeation device was used as the basis for dynamic calibration, against which the results of the static calibration were compared. The experiments involved calibrating an instrument by both dynamic and static procedures as described in the experimental section. Both modified Saltzman and Lyshkow absorbing solutions were used. A minimum of five calibration points were generated over the 0 to 0.4 ppm (modified Saltzman) and 0 to 0.25 ppm (Lyshkow) range. (No significance should be attached to the use of different ranges with the two absorbing solutions; equal ranges could have been used.) The millivolt response was plotted against $NO_2$ concentration for the dynamic and

static procedures, and the data were fitted to a straight line by the method of least squares. The results are shown in Figures 2 and 3 for the Lyshkow and the modified Saltzman absorbing solutions, respectively; equations for the calibration curves are also included.

The results show that, with both absorbing solutions, the slopes of the static calibration curves were significantly different from those obtained by dynamic calibration. The dynamic slope in Figure 2 is 15 percent less than the static slope. A repeat of this experiment using a different Technicon IV instrument showed a difference of twice the first values (-31 percent). To determine if all of the $NO_2$ was being absorbed in the dynamic calibration, the air vented from the concurrent solution-air glass contact coils (absorbing system) was sampled using a manual $NO_2$ method[17] that involved placing a midget impinger containing absorbing solution in line. The results showed that 0.08 ppm of the $NO_2$ from a 0.25 ppm calibration atmosphere was in the vented air. Thus, the collection efficiency of this second instrument was approximately 70 percent (and presumably higher with the first instrument but still less than the assumed 100 percent). Pierce[18] has shown that the design dimensions of this type of absorption system have a critical effect on collection efficiency.

In the experiment shown in Figure 3, where yet another Technicon IV instrument was used, the dynamic slope is 17 percent greater than the static slope. Thus, the above relationship of the slopes has been reversed.

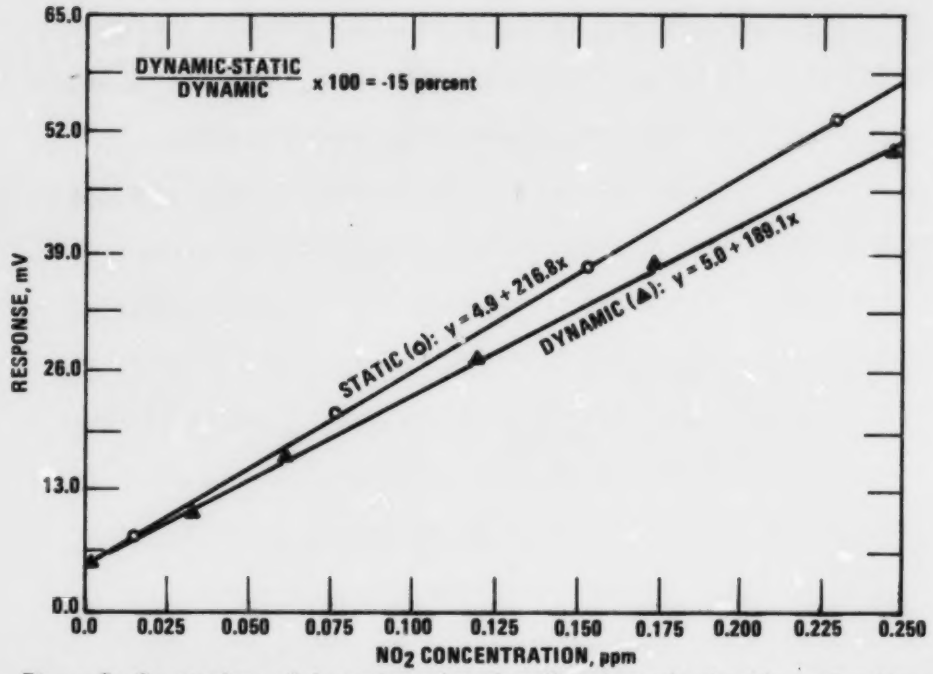


Figure 2. Comparison of dynamic and static calibration using Lyshkow absorbing solution.

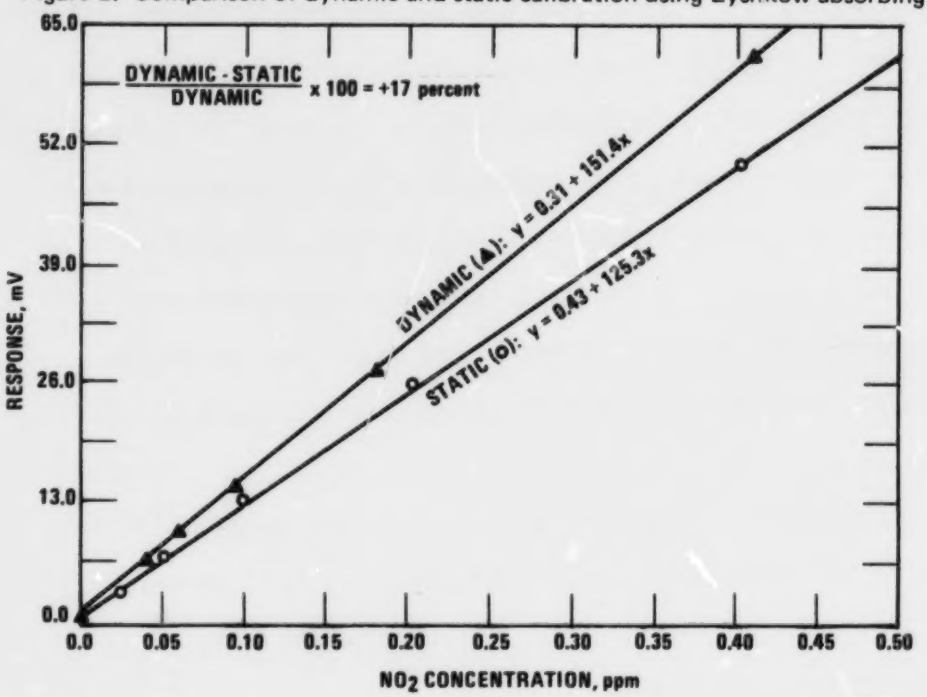


Figure 3. Comparison of dynamic and static calibration using modified Saltzman absorbing solution.

All of these results suggest that differences in dynamic and static calibrations can depend on individual instrument design. Because different makes of instruments would invariably possess a variety of absorber designs as well as differing solution and air flow rates (all of which would affect $NO_2$ collection to different degrees), it would be virtually impossible to develop a universal correction factor that would make static and dynamic calibrations agree, thus allowing use of static calibration in a standard method. Higuchi,[19] for example, performed dynamic and static calibrations on 12 different analyzers and found that differences varied significantly from instrument to instrument.[19]

Dynamic calibration eliminates collection efficiency errors and the use of stoichiometric factors (which might be incorrect) because, whatever the errors are, they would be the same in sampling and calibration and therefore cancel. Accordingly, dynamic calibration using a reliable $NO_2$ source was specified as the calibration procedure in the method write-up. See section 8 of the Appendix for details.

## RESPONSE TIME

In developing a continuous colorimetric method, rapid color formation is important because the rate of color formation affects the response time of the instrument. When analyzed manually, both the modified Saltzman and the Lyshkow absorbing solutions reached 97 percent of full color development after 3 minutes. With the Technicon IV, however, both absorbing solutions required 15 minutes to reach the same level of color development.

Thus, the rapid response time reported for the Lyshkow absorbing solution, and the potentially faster response time of the modified Saltzman solution, were not obtained with the continuous instrument tested.

## INTERFERENCES

No laboratory experiments were carried out to determine chemical interferences in this method because considerable work has already been done. Saltzman[12] recognized ozone as a negative interferent in the manual procedure. Baumgardner et al.[20] and Clark et al.[12] quantitated this effect for the continuous procedure and found the interference to depend on the $O_3/NO_2$ ratio; ratios of 1:1, 2:1, and 3.5:1 produced interferences of 5, 19, and 38 percent, respectively. Thomas[13] showed that alkyl nitrites are positive interferents. The concentration of this species in ambient air is probably low enough for the interference to be minor, however. A 30:1 ratio of $SO_2$ to $O_3$ slowly bleaches the color of the dye in the manual procedure,[12] and this effect may be applicable to the continuous procedure. In practice, the interference would probably be very minor because of the high ratio required.

Ozone, therefore, can be a significant interferent in the continuous colorimetric method.

## PURITY OF NEDA

Midwest Research Institute, during its work under an EPA contract to collaboratively test methods for measuring $NO_2$ in ambient

air, investigated the effects of NEDA purity on the wavelength of maximum absorbance ($\lambda$ max) of the dye developed in a diazotization-coupling type of reaction.[22] The contractor found that aqueous NEDA with one major absorption peak at 320 nm, over the range 260-400 nm (Figure 4), consistently gave a $\lambda$ max of 542 nm. The method specified maximum absorbance at 540 nm. NEDA showing minor absorption peaks in addition to the major peak at 320 nm (Figure 5) shifted the $\lambda$ max to 530 nm. This shifting of the $\lambda$ max was undoubtedly caused by impurities in the NEDA that absorb light between 260 and 320 nm.

Based on these findings, a specification for purity of NEDA was developed (see Appendix, section 6.3).

WAVELENGTH OF MAXIMUM ABSORBANCE

The wavelength of maximum absorbance of the dye in a colorimetric method should be the same as the wavelength utilized in calibration and measurement. If these differ significantly, a loss in sensitivity will result. The colorimeter in the Technicon IV instrument uses a 560 nm optical filter.

The $\lambda$ max of the Lyshkow and modified Saltzman absorbing solutions was determined manually for comparison with the 560 nm value. This was done by adding a $NaNO_2$ solution to the two absorbing solutions, prepared according to the specifications in the Appendix - which include using pure NEDA, allowing 15 min for color development, and determining $\lambda$ max as described in the experimental section. The results in Figures 6 and 7 show a $\lambda$ max of 542 and 547 (540-553) nm

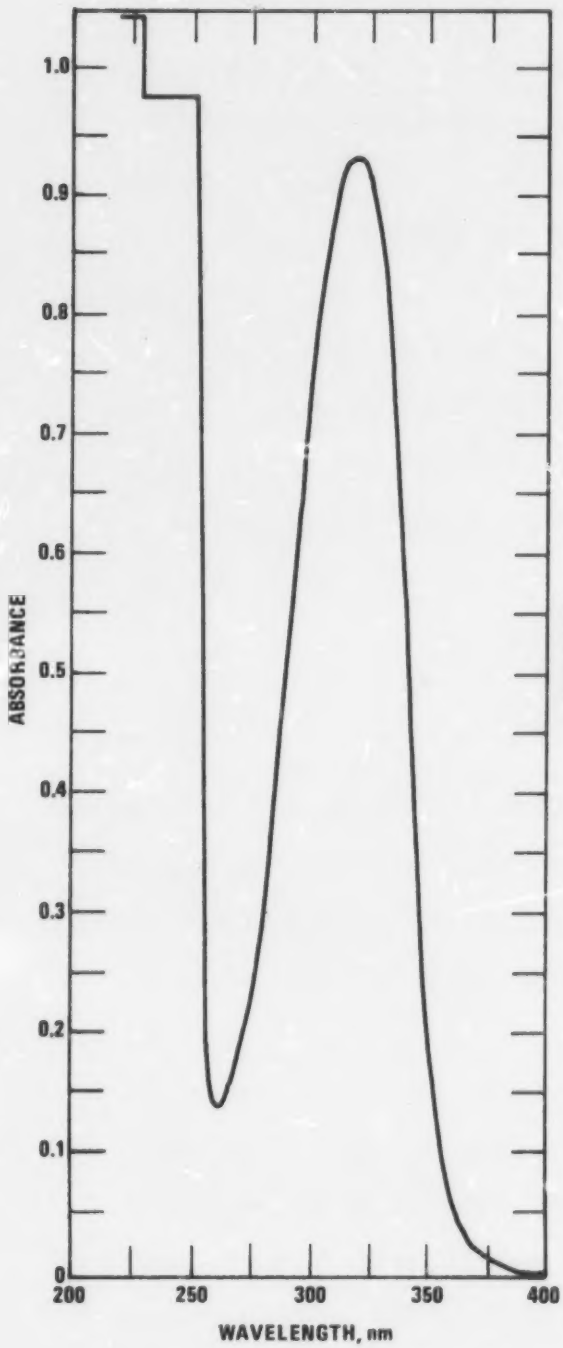


Figure 4. Typical scan of unreacted NEDA solutions that gave a broad absorption peak at 320 nm.[22]

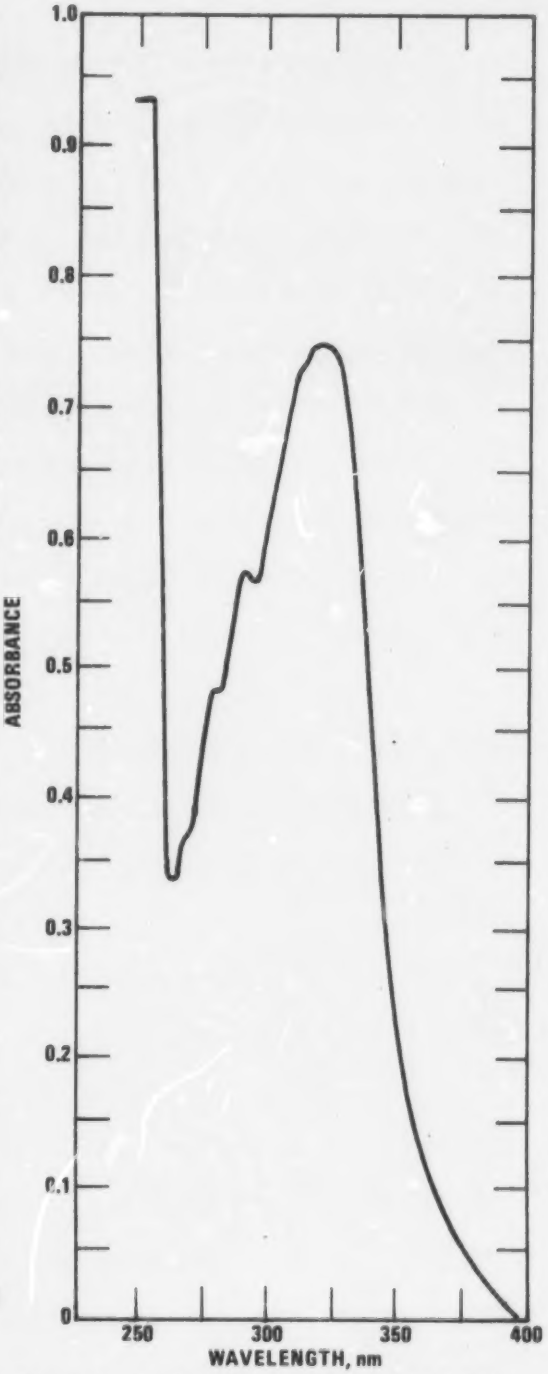


Figure 5. Typical scan of unreacted NEDA solutions that gave minor absorption peaks, as well as a major absorption peak at 320 nm.[22]

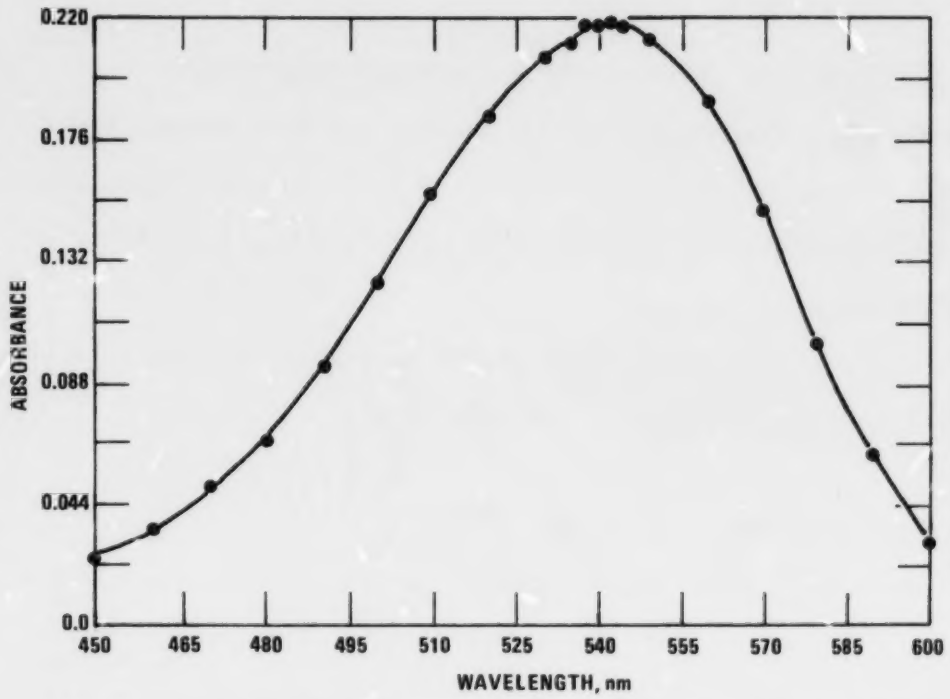


Figure 6. Wavelength of maximum absorbance for Lyshkow absorbing solution.

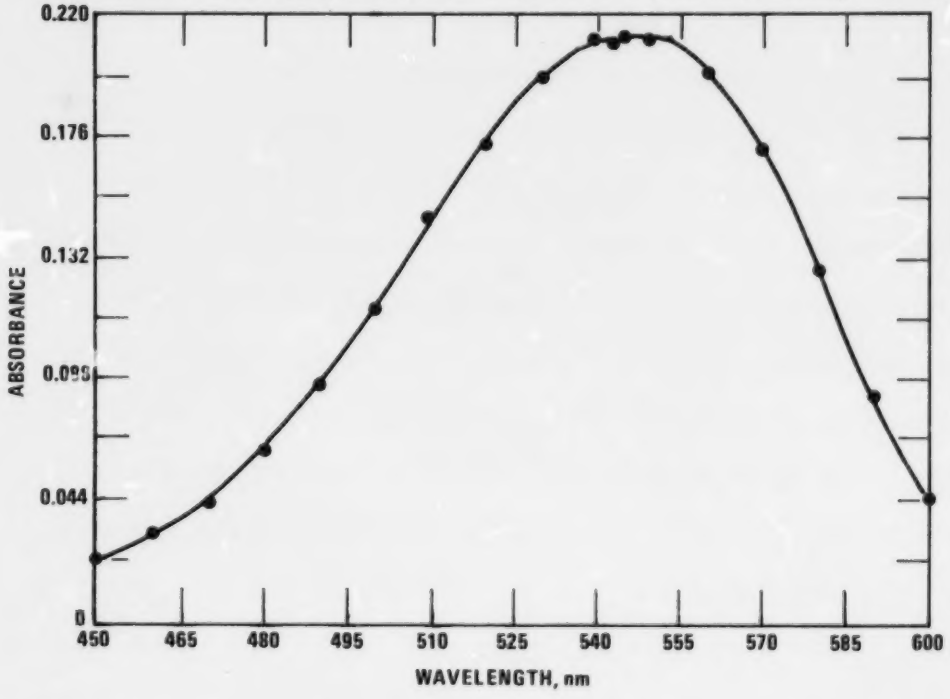


Figure 7. Wavelength of maximum absorbance for modified Saltzman absorbing solution.

for the Lyshkow and the modified Saltzman absorbing solutions, respectively. From these data, measurement at 560 nm amounts to a loss in sensitivity of approximately 13 and 7 percent, respectively, for the two solutions. (Use of impure NEDA caused a larger loss in sensitivity.)

Thus, for optimum sensitivity, instruments using these solutions should use a 540 nm filter in the colorimeter.

## STABILITY OF ABSORBING SOLUTIONS

The use of a continuous colorimetric method often involves exposure of the absorbing solution to changing environmental conditions that could affect stability. Exposure can occur in transporting solutions from the laboratory to a field monitoring site and during operation of the instrument in the field. Accordingly, the effect of subjecting the Lyshkow and the modified Saltzman absorbing solutions to simulated ambient temperature conditions was measured. The experiments involved placing volumetric flasks of the solutions in a constant temperature bath, protected from light to simulate use conditions, and varying the temperature over a 24-hr period as follows: 4 hr at 27 $^{o}$C (81 $^{o}$F), 4 hr at 30 $^{o}$C (86 $^{o}$F), and 16 hr at 22 $^{o}$C (72 $^{o}$F). This cycle was repeated every 24 hrs. The effect on stability was determined by measuring the net absorbance of the solutions (absorbance developed by adding a $NaNO_2$ solution - blank absorbance) as a function of time. These

same measurements were made on solutions exposed to two laboratory conditions at 22 $^{o}$C--storage on the laboratory bench top exposed to light and storage in the dark.

The net absorbance data were plotted, on an expanded scale, as a function of time for all three conditions and fitted to a straight line by the method of least squares. The results are shown in Figures 8 and 9 for the Lyshkow and the modified Saltzman absorbing solutions, respectively. The absorbance of the blanks as a function of time was plotted separately (see Figures 10 and 11).

The net absorbance, which is what the instrument measures, shows no significant change under any of the three conditions up to the limits of the study (14 days for temperature stability and 27 days for storage conditions). The largest change was an increase of 0.004 absorbance units when the solutions were stored exposed to light. This change was below the lower detectable limit of the instrumental procedure, and, therefore, was not significant in terms of the method.

The absorbance of the blank for the modified Saltzman solution showed no significant change under any of the exposure conditions after 27 days. The Lyshkow solution showed an increase in absorbance of 0.02 after the same period of exposure. Because the net absorbance was not significantly increased, however, this color development by the blank does not appear to represent a potential source of error in the method.

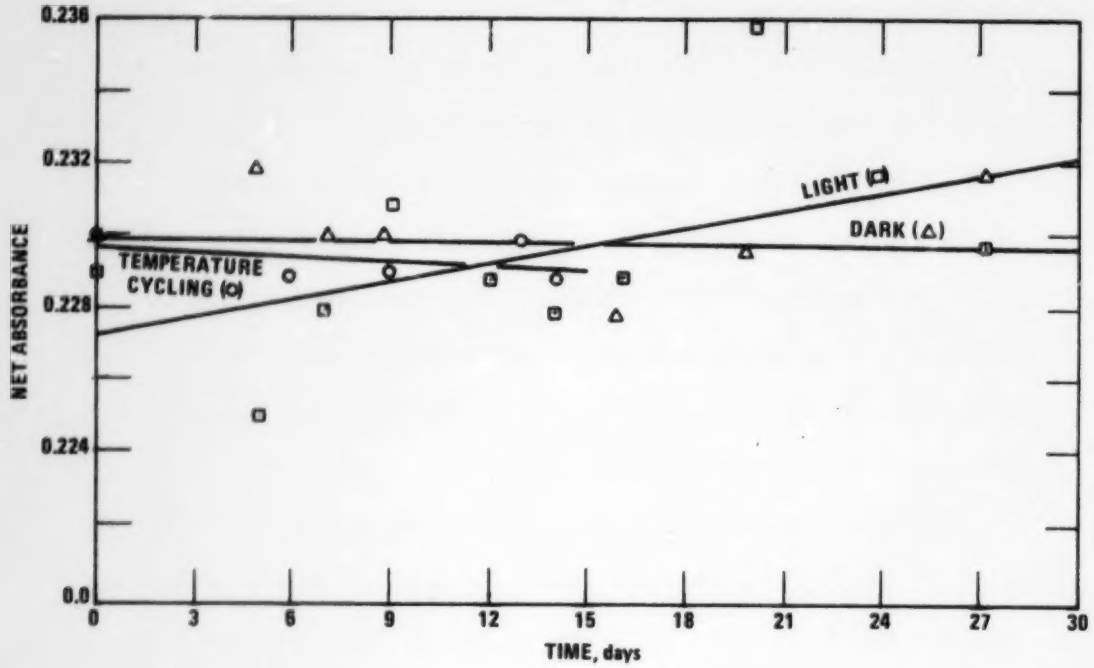


Figure 8. Stability of net absorbance developed by Lyshkow absorbing solution.

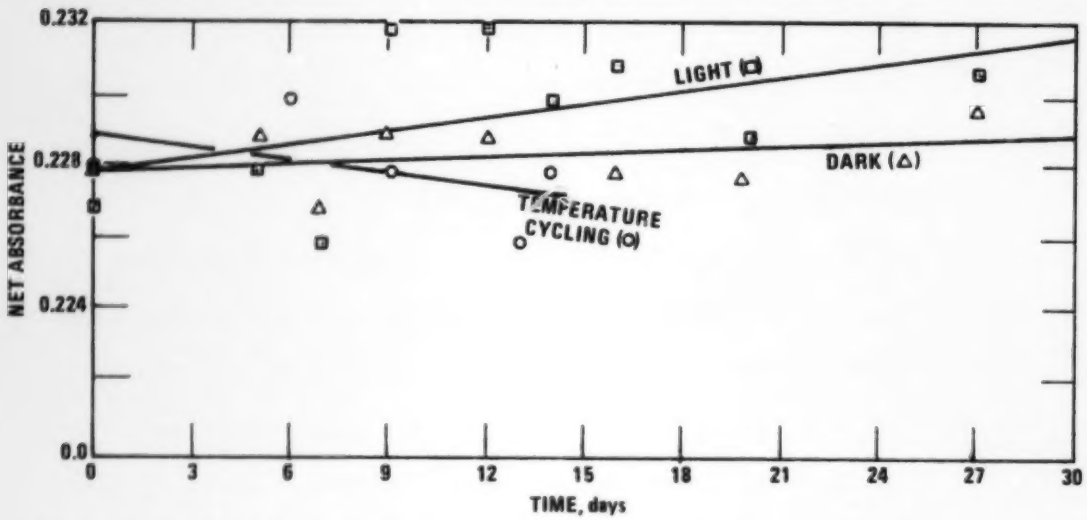


Figure 9. Stability of net absorbance developed by modified Saltzman absorbing solution.

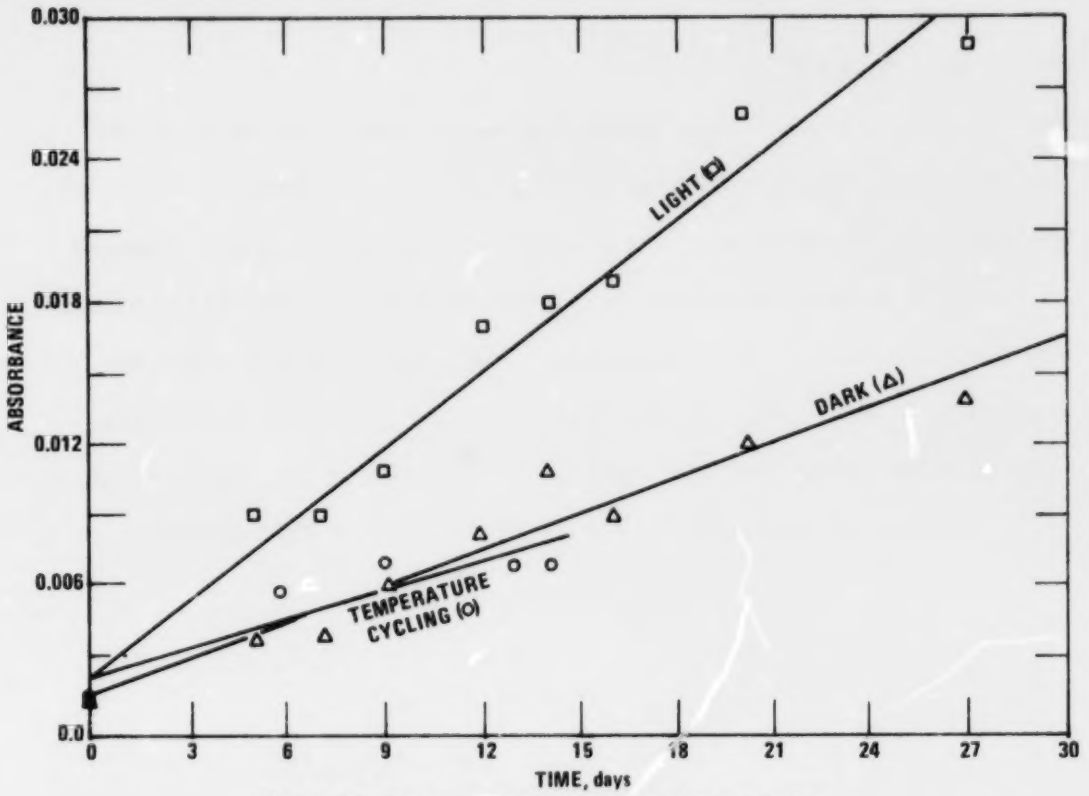


Figure 10. Stability of Lyshkow absorbing solution.

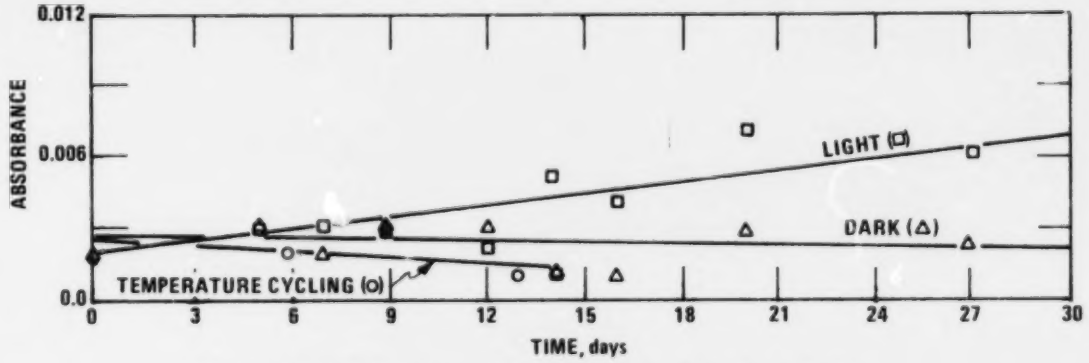


Figure 11. Stability of modified Saltzman absorbing solution.

USE OF WETTING AGENT

Because Lyshkow[15] recommended the use of a wetting agent in the absorbing solution, a non-ionic wetting agent (0.1 percent Triton X-100) was added to the solution. The addition of the wetting agent produced an unstable recorder response (very high noise level) when this solution was used to sample an $NO_2$ atmosphere. The unstable response was undoubtedly caused by air, in the foam produced by the addition of the wetting agent, affecting the signal from the colorimeter. Accordingly, it is recommended that wetting agents not be used in this method.

# IV. FUTURE WORK

In spite of the limitations of the procedure, it was decided to complete the standardization process and subject the continuous colorimetric method to a collaborative test. Because the method is likely to continue in wide use for some time, it should be used to its fullest capabilities; a collaborative test will help to define these capabilities.

The collaborative test was carried out during the week of July 29, 1974, under EPA contract 68-02-1363.[22] Analysis of the data and reporting of the results are in progress.

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# APPENDIX.

# TENTATIVE METHOD FOR DETERMINATION OF NITROGEN DIOXIDE IN ATMOSPHERE* (CONTINOUS COLORIMETRIC PROCEDURE)

October 1974

*A tentative method is one which has been carefully drafted from available experimental information, reviewed editorially within the Methods Standardization and Performance Evaluation Branch and has undergone extensive laboratory evaluation. The method is still under investigation and therefore is subject to revision.

1. Principle and Applicability

1.1 The method is based on the reaction of $NO_2$ in acid media to produce nitrous acid (HONO) with subsequent diazotization and coupling. $NO_2$ in ambient air is continuously absorbed in a solution of diazotizing-coupling reagents to form an azo-dye that absorbs light, with a maximum absorbance at approximately 540 nm. The transmittance, which is a function of the $NO_2$ concentration, is measured continuously in a colorimeter, and the output is read on a recorder or a digital voltmeter.

1.2 The method is applicable to the continuous determination of nitrogen dioxide in ambient air.

2. Range and Sensitivity

2.1 Typical ranges are 0 to 470 $\mu g/m^3$ (0 to 0.25 ppm), 0 to 940 $\mu g/m^3$ (0 to 0.50 ppm), and 0 to 1880 $\mu g/m^3$ (0 to 1.0 ppm). Beer's law is obeyed throughout this range.

2.2 For optimum sensitivity, the wavelength specification of the filter in the colorimeter should correspond to the wavelength of maximum absorbance of the dye. This may not be the case in some instruments. Therefore, the dye should be scanned and the wavelength of maximum absorbance determined. If the filter is not within ± 10 nm of the wavelength maximum obtained by scanning the dye, the filter should be replaced by one that meets this specification.

The stability of both solutions is unchanged after temperature cycling to simulate ambient conditions (up to 30°C for 4 hours per day for 7 days).

5. Apparatus

5.1 Continuous $NO_2$ analyzer. Sample air is drawn through a gas/liquid contact column at an accurately determined flow rate concurrent to a controlled flow of absorbing reagent. The sample inlet line prior to the absorber column should be constructed of either glass or Teflon. The absorber column must be carefully designed and properly sized because $NO_2$ is somewhat difficult to absorb. The colored solution is passed through a colorimeter where the transmittance is measured continuously.

5.1.1 Probe. Glass or Teflon, with inverted polypropylene or glass funnel at the end.

5.1.2 Installation. Instruments should be installed on location and demonstrated, preferably by the manufacturer, to meet or exceed the specifications described in the addendum.

5.2 Calibration. The calibration apparatus and its use is described in Section 8. Additional components follow:

5.2.1 Dilution air and flushing air (or $N_2$). This can be compressed (house) air or cylinder air. It should be purified by passing through silica gel for drying, and through activated charcoal (6-14 mesh) and molecular sieve (6-16 mesh, type 4A) to remove any $NO_2$ and hydrocarbons.

5.2.1.1 Purity. Test the purity of the dilution and flushing air by operating the instrument in the zero mode until a stable baseline is obtained. Connect the dilution or flushing air tube to the air intake of the gas/liquid contact column and operate the instrument in the ambient mode. If the response changes by more than twice the noise level, the air is impure. Correct before proceeding.

5.2.2 Flow meters. One each with ranges of 0-100 $cm^3$/min , 0 to 1 ℓ/min. and 0 to 20 ℓ/min is required.

5.2.2.1 Calibration. This can be accomplished with a bubble flow meter or a wet test meter. With a stopwatch, determine the rates of air flow ($cm^3$/min) through the flow meter at a minimum of four different ball positions. Plot ball positions versus flow rates.

5.2.3 Thermometer. Graduated in $0.1^{o}$ intervals over the range 20 to $30^{o}$ C.

## 6. Reagents

6.1 Sulfanilamide [$4\text{-}(H_2N)C_6H_4SO_2NH_2$]. Melting point $165\text{-}167^{o}$C.

6.2 Sulfanilic Acid Monohydrate, [$4\text{-}(NH_2)C_6H_4SO_3H\cdot H_2O$]. ACS reagent grade. Either the monohydrate or anhydrous form can be used, provided the degree of hydration is known. If the degree of hydration is not known, recrystallize from water and dry over night at $120^{o}$C. [4] This will give the anhydrous material.

3. Interferences

3.1 Recent studies[1] have shown that ozone can produce a negative interference, the magnitude of which depends on the $O_3$ to $NO_2$ ratio. In the study cited, $O_3/NO_2$ ratios of 1:1, 2:1 and 3.5:1 produced interferences of 5, 19, and 38 percent, respectively.

3.2 Alkyl nitrites are positive interferents. The magnitude of the interference depends on the structure of the alkyl nitrite.[2]

3.3 A 30: 1 ratio of $SO_2$ to $NO_2$ slowly bleaches the color of the azo-dye in the manual procedure,[3] and this effect may be applicable to the continuous procedure.

4. Precision, Accuracy and Stability

4.1 No data are available on precision and accuracy.

4.2 Air bubbles can accumulate in the optical cell and will cause an erratic response. This instability can be minimized by increasing the air and solution flow rates. The ratio of the air to solution flow rate should be maintained at the value recommended by the manufacturer (see Section 7).

4.3 The modified Saltzman absorbing reagent (Section 6.8.1) is stable for 1 month under laboratory conditions (22°C; exposed to light). The Lyshkow solution (Section 6.8.2) develops an absorbance of approximately 0.02 after 1 month under laboratory conditions. The net absorbance (absorbance developed by adding a $NO_2^-$ solution - blank) is unchanged after 1 month.

6.3 N-(1-Naphthyl)-ethylenediamine dihydrochloride (NEDA). An aqueous solution should have one absorption at 320 nm. over the range 260-400 nm.

6.4 Tartaric Acid. ACS Reagent grade.

6.5 Glacial Acetic Acid. ACS Reagent grade.

6.6 2-Naphthol-3-6-disulfonic acid disodium salt. [$HOC_{10}H_5(SO_3Na)_2$] Technical Grade. This compound is also known by its trivial name, R-salt.

6.7 Nitrite-free distilled water. Mix the water with absorbing solution. Absence of any visible pink coloration indicates that the water is of acceptable quality. If the solution turns pink, redistill the water in an all-glass still after adding a crystal of potassium permanganate and barium hydroxide.

6.8 Absorbing Solutions. Either the modified Saltzman [5] solution or the Lyshkow [6, 7] modification of the Saltzman solution can be used.

6.8.1 Modified Saltzman absorbing solution. 0.5 percent sulfanilic acid, 5.0 percent acetic acid, 0.005 percent NEDA. For 1 liter of solution prepare as follows: dissolve 5.52 g of sulfanilic acid monohydrate (or 5.00 g of the anhydrous material) in hot distilled water and allow to cool to room temperature. Add 50 ml of glacial acetic acid followed by 0.050 g of NEDA. Dilute to 1 liter with distilled water.

6.8.2 Lyshkow solution. 0.15 percent Sulfanilamide, 1.5 percent Tartaric acid, 0.005 percent NEDA and 0.005 percent 2-Naphthol-3,6-disulfonic acid disodium salt. For 1 liter of solution, dissolve 15.0g of

tartaric acid, 1.50 g sulfanilamide, 0.050 g of 2-naphthol-3,6-disulfonic acid disodium salt, and 0.050 g NEDA in 500 ml of distilled water. Dilute to 1 liter with distilled water.

## 7. Procedure

Allow the instrument to warm-up in accordance with the manufacturer's instructions and until a stable baseline is obtained. Turn pumps on and adjust the air and absorbing reagent flow rates and their ratio to the recommended values. Verify the air flow rate by measurements with the 1 ℓ/min flow meter. Calibrate the instrument as described in Section 8.

## 8. Calibration

8.1 General Description. A dynamic calibration is carried out by generating synthetic atmospheres from the output of a reliable $NO_2$-permeation device and determining the instrument response. Instrument response is then plotted against $NO_2$ concentration to obtain a calibration curve.

8.2 $NO_2$-Permeation Device. Obtain or prepare a reliable $NO_2$-permeation device with a permeation rate of approximately 1.0 $\mu g NO_2$/min. The following precautions must be observed in preparing $NO_2$-permeation devices:

1. The $NO_2$ used to fill the device must be dry. [8]
2. The filling operation must be carried out in a dry atmosphere to ensure that water is not introduced when the tube is filled.

3. The $NO_2$ should be pure, assay 99 percent or greater.

4. All seals in the device should be free of leaks.

5. The permeation rate should be checked gravimetrically as follows:

a. Allow the device to reach temperature equilibrium in the $NO_2$-atmosphere generation system (Section 8.3). This will be attained over-night, in most cases.

b. Weigh the device periodically and record the time. (Transport the device from the atmosphere generation system to the balance area in a dessicator.)

c. All weighings should be carried out at the same relative humidity $\pm$ 10 percent. The time of exposure of the device to the atmosphere during weighing should be constant ($\pm$ 30 sec.) from weighing to weighing. This technique cancels any weight gain caused by moisture - $NO_2$ reactions at the effusing surface and gives a reliable measure of the $NO_2$-weight loss.

d. The time interval between weighings will depend on balance sensitivity. With a sensitivity (standard deviation at the mass being weighed) of 40 µg, weighing at 24-hour intervals will produce reliable weight losses.

e. Plot device weight (in micrograms) on the y-axis versus cumulative time (in minutes) on the x-axis. Obtain sufficient data (at least five well-spaced points) to establish the slope of the line, which is the permeation rate in µg/min. Determine the slope algebraically or by regression analysis.

f. The permeation rate should be constant and in reasonable agreement with the suppliers or other previous valve.

8.3 $NO_2$-Atmosphere-Generation System. This consists of an $NO_2$-permeation device contained in a water-jacketed condenser which is connected to a constant-temperature bath. A homogenous $NO_2$ in air atmosphere is produced by flushing the $NO_2$, effusing from the calibrated $NO_2$-permeation device, into a mixing bulb where it is further diluted with dilution air. Figure A-1 shows a diagram of this system with suggested specifications for the component parts. The following key specifications must be met to ensure the generation of reliable calibration atmospheres:

8.3.1 Temperature control must be maintained to within $\pm$ 0.1° C. of a fixed value.

8.3.2 Flushing and dilution air. These must be dry and free of $NO_2$ (see section 5.2.1).

8.3.3 A Kjeldahl connecting bulb with a volume of at least 150 $cm^3$ is required to obtain adequate mixing of $NO_2$ and dilution air.

8.3.4 Connections that are in contact with $NO_2$ must be of glass or Teflon. Rubber tubing may be used for flushing and dilution air connections. Tygon tubing should not be used. Systems for preparation of calibration atmospheres have been described in detail by O'Keeffe and Ortman;[9] Scaringelli, et al.;[10] and Scaringelli, Rosenberg, and Rehme.[4] Commercial calibration systems using the permeation tube technique are now available.

8.4 $NO_2$ Atmospheres. Allow the $NO_2$ atmosphere generation system to equilibrate for at least one hour with flushing and dilution air flowing. Generate a calibration gas equal to 80 $\pm$ 5% of full scale by adjusting the dilution flow rate. Calculate the exact concentration from the following relationship:

$$C = \frac{P \times 10^3}{D + F} \qquad \text{(A-1)}$$

where:

C = $NO_2$ concentration, $\mu g/m^3$

P = $NO_2$ permeation rate, $\mu g/min.$

F = Flushing air flow rate, $\ell/min.$

D = Dilution air flow rate, $\ell/min.$

$10^3$ = Factor to convert liters to cubic meters.

Sample the atmosphere until a stable response is obtained and record the response. Generate four additional concentrations of approximately 10, 20, 40, and 60 percent of full scale and determine the response. (The $NO_2$ permeation rate and highest workable dilution air flow rate may necessitate a higher initial concentration.)

8.5 Other reliable dynamic procedures for generating $NO_2$ can be used. For example, gas phase titration of excess NO with $O_3$, [11] and analyzed cylinders of $NO_2$ in $N_2$ that are stable. [12]

8.6 Calibration Curve. Plot the concentration of $NO_2$ in micrograms/cubic meter (x - axis) against instrument response (y - axis), and draw the line of best fit. Some instruments are designed to give a linear and some a non-linear response.

8.7 Frequency of Calibration. The calibration should be checked daily by spanning the calibration curve at 80 percent of full scale. Spanning by generation of a dynamic standard is preferred. However, if field use of the instrument makes this impractical, a static-calibration check can be carried out by adding a solution of nitrite ion, $NO_2^-$ (as $NaNO_2$), to the absorbing solution to generate the dye. (Most instruments have a static calibration mode through which solutions can be introduced.) CAUTION: Static and dynamic calibrations may not agree; therefore, if static spanning is to be used, a static reference point should be established at the time of calibration.

## 9. Calculations

9.1 $NO_2$ Concentration. This is read directly from the calibration curve. A 1-hour or longer average concentration is reported. Electronic or electro-mechanical integration, equal area averaging, a planimeter, paper weighing techniques, or the average of a digital output can be used to obtain the average concentration.

9.2 The $NO_2$ concentration can be converted to ppm as follows:

$$\text{ppm } NO_2 = \mu g\ NO_2/m^3 \times 5.32 \times 10^{-4} \qquad \text{(A-2)}$$

9.3 Air Volume. The volume of air sampled is not corrected to standard temperature and pressure because of the uncertainty associated with average temperature and pressure valves.

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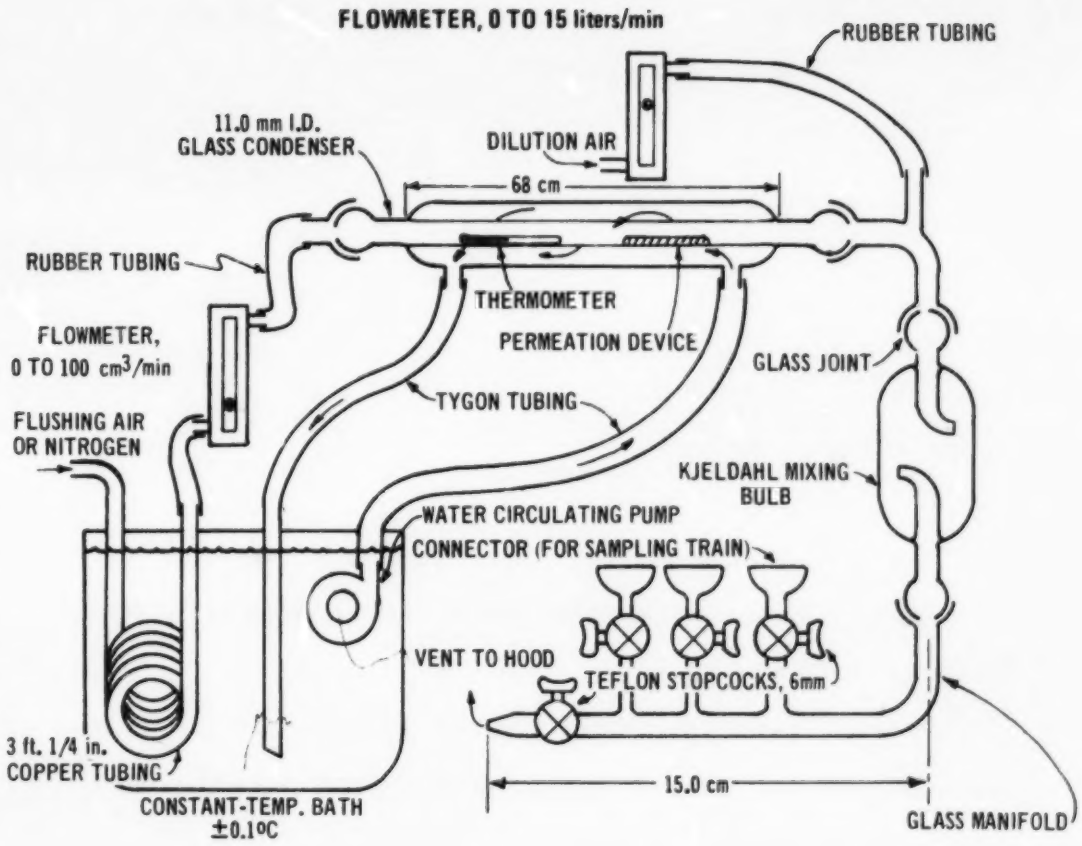


Figure A-1. Typical $NO_2$ atmosphere generation system.

## ADDENDUM

A. Performance Specifications for Continuous Colorimetric Atmospheric Analyzers.

| | |
|---|---|
| Range | Multiple |
| Noise | 0.005 ppm |
| Lower Detectable Limit | 0.01 ppm |
| Zero Drift | |
| 12 Hour | ± 0.02 ppm |
| 24 Hour | ± 0.02 ppm |
| Span Drift - 24 hour | 0.02 ppm |
| Lag Time | 20 minutes |
| Rise Time, 95 percent | 15 minutes |
| Fall Time, 95 percent | 15 minutes |

B. Definitions of Performance Specifications.

Range - Minimum and maximum concentrations which the system shall be capable of measuring.

Noise - Spontaneous, short-duration deviations in the instrument output about the mean output, which are not caused by input concentration changes.

Lower Detectable Limit - The minimum pollutant concentration which produces a signal of twice the noise level.

Zero Drift - The change in instrument output over a stated time period of unadjusted continuous operation when the input concentration of pollutant is zero.

Span Drift - The change in instrument output over a stated time period of unadjusted continuous operation when the input pollutant concentration is a stated upscale value.

Lag Time - The time interval between a step change in input concentration at the instrument inlet to the first observable corresponding change equal to twice the noise in the instrument output.

Rise Time - The time interval between initial response and 95 percent of final response after a step increase in input concentration.

Fall Time - The time interval between initial response and 95 percent of final response after a step decrease in input concentration.